TABLE II

YIELDS AND PROPERTIES OF ALKYL HYDROPEROXIDES

Alkyl Group	Yield, %	M.P. °	(OOH)[10,11] Analysis, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-Dodecyl	55.8	12–13	95	$C_{12}H_{26}O_2$	71.28	71.26	12.87	12.42
n-Tetradecyl	42.4	29–30.5	92	$C_{14}H_{30}O_2$	73.05	73.58	13.05	12.56
n-Hexadecyl	31	42–44	98.8	$C_{16}H_{34}O_2$	74.42	74.24	13.18	13.17
n-Octadecyl	8.9	49–50	100	$C_{18}H_{38}O_2$	75.39	74.81	13.25	13.00

hexadecyl peroxide (2.5 g.), and octadecyl methanesulfonate (17 g.), respectively.

Tetradecyl peroxide melted at 36.5° and gave an infrared spectra which had only carbon-hydrogen and carbon-oxygen peaks.

Anal. Calcd. for $C_{28}H_{58}O_2$: C, 78.87; H, 13.61. Found: C, 78.58; H, 13.61.

Hexadecyl peroxide melted at 44–46° and gave a similar spectra to tetradecyl peroxide.

Anal. Calcd. for $C_{32}H_{66}O_2$: C, 79.67; H, 13.69. Found: C, 79.00; H, 13.43.

The alkaline filtrate from the original precipitate was diluted with water (100 ml.) and extracted twice with 125-ml. portions of hexane. Concentration of the hexane extract gave impure dodecyl peroxide (4 g.) and unreacted tetradecyl methanesulfonate (3 g.) and hexadecyl methanesulfonate (4 g.) respectively.

The dodecyl peroxide was difficult to purify. The principal contaminations based on the infrared spectra were the corresponding methanesulfonate and aldehyde.

The basic solution was cooled to 0° and made slightly acid with concentrated hydrochloric acid. Extraction with three 125-ml. portions of hexane followed by removal of the solvent under reduced pressure gave an oil which, in the case of tetradecyl, hexadecyl, and octadecyl hydroperoxides, solidified at room temperature. Further purification was accomplished by dissolving the oil (10 g.) in absolute methanol (100 ml.) containing potassium hydroxide (20 g.), cooling the resulting solution, and then adding water (25 ml.). Extraction with two 30-ml. portions of hexane was followed by acidification of the methanol solution. Three extractions with 30-ml. portions of hexane followed by removal of the solvent gave the hydroperoxide. The properties of these compounds and yields are listed in Table II.

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(10) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, 19, 976 (1947).

(11) A. I. Vogel, *Elementary Practical Organic Chemistry, Part III, Quant. Org. Anal.*, Spottiswoode, Ballantyne and Co. Ltd., London, 1958, p. 836.

[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION[1]]

Preparation of Some Vinyl Alkyl Pinates[2]

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Some monoalkyl pinates, 2,2-dimethyl-3-(alkoxycarbonyl)cyclobutaneacetic acids and alkyl 2,2-dimethyl-3-(carboxy)-cyclobutaneacetates, were vinylated by the vinyl interchange method of Adelman. Vinyloxycarbonyl forms of the ethyl, *n*-butyl, 2-ethylhexyl, and hydronopyl mono esters, and vinyl acetate forms of the ethyl, *n*-butyl, and 2-ethylhexyl mono esters were prepared and characterized. Divinyl pinate and vinyl 2-ethylhexyl phthalate are reported also. The preparation of these esters by vinyl interchange is more satisfactory than by the Reppe procedure.

A study concerned with the internal plasticization of polyvinyl chloride led to the preparation of a number of vinyl alkyl pinates.[3]

Schildknecht[4] stated that dibasic acid monovinyl and divinyl esters are generally difficult to prepare. Adelman[5] reported the preparation of vinyl octyl phthalate and vinyl adipate, presumably monovinyl, by vinyl interchange reaction with vinyl acetate.

Adelman presented evidence to show that esters do not undergo vinyl interchange, *e.g.* only the free carboxyl group of monooctyl phthalate reacted with vinyl acetate.

The synthesis of a number of monoalkyl pinates, the alkyl acetate and the alkyloxycarbonyl forms, is reported in another paper.[6] Both types of monoethyl, -*n*-butyl, -2-ethylhexyl, and -hydronopyl[7] pinates were prepared. The preparation of the vinyl esters of these half esters are reported in this paper, excepting vinyl 2,2-dimethyl-3-(hydronopyloxycarbonyl)cyclobutane acetate.

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13–18, 1959.

(3) In cooperation with Dr. C. S. Marvel, University of Illinois, under contract with the U. S. Department of Agriculture.

(4) C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley & Sons, Inc., New York, 1952, p. 382.

(5) R. L. Adelman, *J. Org. Chem.*, 14, 1057 (1949).

(6) J. B. Lewis and G. W. Hedrick, *J. Org. Chem.*, 24, 1870 (1959).

(7) J. P. Bain, *J. Am. Chem. Soc.*, 68, 638 (1946).

The method of Reppe[8] proved unsatisfactory for the preparation of these mixed esters with the conditions employed. However, vinylation of the monoesters was accomplished in good yields by use of vinyl acetate and the vinyl interchange procedure of Adelman[5] with a slight modification which consisted of washing the vinyl acetate free esterification mass to remove the mercury catalyst and acidic components. This additional step decreased the still residue.

A small amount of divinyl ester was always formed during the reaction of monoalkyl pinates with vinyl acetate. This is in contrast to Adelman's hypothesis that esters do not react with vinyl acetate under the conditions employed. However, in a vinyl interchange reaction as the reaction proceeds the acetic acid concentration builds up. When this occurs transesterification can take place, thereby liberating some free acid which then is available for vinylation. This was demonstrated by mixing vinyl acetate, diethyl pinate, and acetic acid using the conditions of the vinyl interchange reaction. One to two per cent of the diester was vinylated in this reaction.

Divinyl pinate was prepared for characterization and comparison with material obtained from the other vinylations. The esters and physical properties are given in Table I. Samples of the vinyl esters were reduced and the properties of the saturated esters were determined. Vinyl 2-ethylhexyl phthalate was prepared for polymerization and comparison with the vinyl pinates. The results are included in this paper since the physical properties are somewhat different from those reported previously.

EXPERIMENTAL

Vinyl 2,2-dimethyl-3-(ethoxycarbonyl)cyclobutane acetate. Reppe process. 2,2-Dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid,[9] 214 g. (1 mole), and zinc oxide, 15.7 g. (0.19 mole), were added to 250 ml. toluene and heated to reflux to remove water by trapping in a decanter. The solution was almost clear, although some of the zinc salts remained undissolved. Glacial acetic acid, 13.8 g., was added to clarify completely the solution.

Vinylation was accomplished with acetylene by the Reppe procedure.[8] The product was isolated by washing the toluene solution with dilute sulfuric acid, water and dilute carbonate solution. The solvent was stripped under water aspirator vacuum and the residue distilled using a 24-inch Vigreux column. The following fractions were obtained: (1) 5 ml., 20° to 87.5° (0.4 mm.); (2) 50.1 g., 87.5° to 96° (0.4 mm.); (3) 52 g., 97° (0.5 mm.) to 99° (0.55 mm.). Five ml. of the 2nd and 3rd fractions polymerized violently when 0.3% benzoyl peroxide was added. Both polymers were insoluble in acetone, benzene and methanol indicating cross linking presumably because of the presence of divinyl pinate.

Vinyl interchange reaction. Monoethyl pinate, above, neut. equiv. 214, 455 g. (2.13 moles) was dissolved in 1193 g. (13.9 moles) freshly distilled vinyl acetate (Eastman Organic Chemicals) containing 1.22 g. copper resinate. Mercuric acetate, 9.4 g. (0.029 mole), was dissolved therein while stirring at room temperature and 2.33 g. (0.023 mole) concentrated sulfuric acid was added slowly. The final solution was clear and bright green in color. After standing 72 hr., 10 g. sodium acetate (0.12 mole) was added. The excess vinyl acetate was stripped by water aspirator vacuum maintaining the still residue at 20° to 30°. The crude ester was dissolved in 500 ml. ether. This solution was washed with dilute aqueous sulfuric acid, then two 500-ml. portions of a dilute solution of alkali maintained at *p*H 8 to 9 with sodium hydroxide and soda ash and finally with water. Acidification of the alkaline extract gave 50 g. recovered starting material. Removal of the solvent as above and distillation, bulb-to-bulb, gave 431 grams, b.p. 100°, 1.9 mm. to 1.5 mm., with 30 g., residue. Redistillation at 2 mm. using a 24-inch Vigreux column gave the following fractions: (1) 10 g. up to 106°, (2) 72 g., 106° to 111°, (3) 28 g., 111° to 112°, and (4) 300 g., 112°.

The last three fractions were combined for removal of divinyl pinate by distillation through a 45-cm. column packed with extruded nickel. The results are tabulated as follows, Table I:

TABLE I

DISTILLATION OF CRUDE VINYL 2,2-DIMETHYL-3-(ETHOXYCARBONYL)CYCLOBUTANEACETIC ACID

Fractions	B.P., 2 mm.	Wt. (g.)	Composition,[a] % A	Composition,[a] % B	Hydrogenation[b] Equivalent
1a	104–108	16	95.1	4.9	1.97
2a	108–111	17	95.1	4.9	1.97
3a	111	11	11.1	88.9	1.11
4a	111–113	40	1.8	98.2	1.02
5a	113	21	1.4	98.6	1.01
6a	113	210	1.4	98.6	1.016

Residue 55 g. [a] Calcd., as (A) divinyl pinate, as (B) monovinyl ester. [b] Determined by hydrogenation in acetic acid solution with 5% palladium on carbon catalyst. Platinum oxide gave erroneously high results.

Fractions 4a through 6a were combined and the divinyl ester removed by distillation, using the nickel-packed column at a high reflux ratio. The remainder was distilled at a more rapid rate. A sample of fraction 4a and samples of the final distillate with and without 2% added divinyl pinate were polymerized in bulk with benzoyl peroxide as the initiator. The polymers from 4a and the sample with added divinyl pinate were not soluble in benzene, thus indicating cross linking. It is apparent that divinyl pinate is produced by this vinyl interchange reaction.

Divinyl pinate. In preparation of zinc pinate by reacting zinc oxide and pinic acid in toluene for use as a catalyst in the Reppe process the reaction mass was thick with insoluble zinc pinate. Furthermore, addition of acetic acid did not dissolve the salt. In another experiment the zinc salt from 42.8 g. (0.2 mole) of monoethyl pinate, alkyloxycarbonyl form was prepared and 184 g. (1 mole) of pinic acid added. After vinylation by addition of acetylene as with the half ester above and working up the product 76 g. crude ester was obtained, b.p. 90 to 150°, 1.0 mm. Since the bulk of the material distilled at 130°, it was concluded the product was chiefly monovinyl pinate.

Because of the difficulties obtained by the Reppe process divinyl pinate was prepared by the vinyl interchange method of Adelman. The product was isolated without washing to remove the catalyst and acidic components. From 82 g. pinic acid (0.44 mole) 30 g. (0.126 mole) of good divinyl pinate was obtained by a bulb-to-bulb distillation and finally distillation using an 18-inch column packed with 1/8-

(8) J. W. Copenhaver and M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, Reinhold Publishing Corp., New York, p. 59.

(9) Pinic acid esters used in this work consisted of mixtures of *cis-d*- and *cis-dl*-isomers.[6]

inch glass helices; diethyl ester from reduction, n_D^{20} 1.4457.

Vinyl interchange with vinyl acetate and diethyl pinate. In order to show that an interchange reaction can occur between an ester and vinyl acetate, 121 g. (0.5 mole) of diethyl pinate was treated at room temperature with vinyl acetate using a mercury catalyst as above. In addition 21 ml. glacial acetic acid was added to simulate conditions toward the end of a normal vinyl interchange reaction. The first portion of the distillate, about 10 g., b.p. 100 to 113°, 2 mm., contained vinyl ester which on hydrogenation absorbed 0.008 mole hydrogen. Subsequent fractions combined, 48 g., b.p. 113° to 114°, 2 mm., decolorized bromine in carbon tetrachloride. The last fraction, 4 g., contained no unsaturated compounds.

Vinyl 2,2-dimethyl-3-(n-butoxycarbonyl)- and -3-(2-ethylhexyloxycarbonyl)cyclobutane acetates. Vinylation of 2,2-dimethyl-3-(*n*-butoxycarbonyl)- and -3-(2-ethylhexyloxycarbonyl)cyclobutaneacetic acid was accomplished by the vinyl interchange procedure used for the 3-ethoxycarbonyl derivative. With the higher molecular weight esters the volume of vinyl acetate charged was increased. With the butyl ester 644 g. (7.48 moles) and with the 2-ethylhexyl ester 793 g. (9.22 moles) vinyl acetate were used per mole pinate ester. Because of the higher boiling point of these higher molecular weight esters, isolation to free them of divinyl pinate was easier than with the ethyl ester.

Ethyl, n-butyl, 2-ethylhexyl and hydronopyl 2,2-dimethyl-3-(vinyloxycarbonyl)cyclobutane acetates. Vinylation of ethyl, *n*-butyl, 2-ethylhexyl and hydronopyl 2,2-dimethyl-3-(carboxy)cyclobutane acetates resulted in 70 to 80% yields by reacting the monoesters with vinyl acetate as above. The vinyl acetate was increased for the higher molecular weight esters.

The vinylation of 454 g., (2.12 moles) of monoethyl pinate gave 413 g. crude ester. The results of fractionation using the nickel packed column mentioned before are tabulated in Table II.

In this instance the presence of divinyl pinate was indicated from hydrogenation data. Redistillation gave 355 g. almost pure vinyl ester. The presence of divinyl pinate was observed in all the vinylations made.

Vinyl 2-ethylhexyl phthalate. Because of the instability of mono-2-ethylhexyl phthalate toward distillation the crude mixture containing principally anhydride, mono and diester was vinylated by the vinyl interchange method. Since the physical constants obtained for vinyl 2-ethylhexyl ester differs from the data given by Adelman[5] it is presumed that he used *n*-octyl alcohol in his synthesis.

The results of the characterization of the vinyl esters are tabulated in Table III. Divinyl pinate and vinyl alkyl pinates were reduced and the resulting diethyl esters identified by refractive index and density.[6]

TABLE II

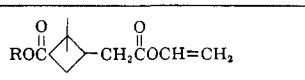
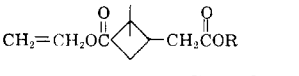
DISTILLATION OF ETHYL 2,2-DIMETHYL-3-(VINYLOXYCARBONYL)CYCLOBUTANE ACETATE

Fractions	B.P., 2 mm.	Wt., g.	Composition,[a] % A	Composition,[a] % B	Hydrogenation Equivalent
1	68 to 104	25	—	—	—
2	105 to 112	48	7.6	92.4	1.078
3	112 to 113	45	1.2	98.8	1.012
4	113	270	0.8	99.2	1.009

[a] Calcd. as (A) divinyl pinate, as (B) monovinyl ester.

TABLE III

VINYL ALKYL PINATES

Vinyl Alkyl Esters	Hydrogenation Equivalent[a]	B.P.	Mm./Hg	n_D^{20}	d^{20}	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
Vinyl Acetates 										
Ethyl	0.99	113	2.0	1.4558	1.0220	$C_{13}H_{20}O_4$	64.98	8.39	64.81	8.39
n-Butyl	0.99	135–136	2.0	1.4569	0.9992	$C_{15}H_{24}O_4$	67.13	9.01	66.82	8.96
2-Ethylhexyl	0.98	142	0.4	1.4594	0.9691	$C_{19}H_{32}O_4$	70.33	9.94	70.52	9.75
Alkyl Acetates 										
Ethyl	1.009	113	2.0	1.4556	1.0200	$C_{13}H_{20}O_4$	64.98	8.39	64.86	8.47
n-Butyl	0.99	130–134	2.0	1.4560	0.9980	$C_{15}H_{24}O_4$	67.13	9.01	66.82	8.96
2-Ethylhexyl	1.007	138	0.1	1.4592	0.9686	$C_{19}H_{32}O_4$	70.33	9.94	70.26	9.83
Hydronopyl	1.004	170	0.1	1.4872	1.0287	$C_{22}H_{34}O_4$	72.89	9.45	72.83	9.54
Others										
Divinyl pinate	1.99	110–112	2.0	1.4667	1.0343	$C_{13}H_{18}O_4$	65.53	7.61	65.46	7.69
Vinyl 2-ethylhexyl phthalate	1.00	144	0.1	1.5008	1.0364	$C_{18}H_{24}O_4$	71.03	7.95	71.25	8.20

[a] Equivalents hydrogen per mole.

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